

# (12) UK Patent Application (19) GB (11) 2 290 548 (13) A

(43) Date of A Publication 03.01.1996

(21) Application No 9511863.4

(22) Date of Filing 12.06.1995

(30) Priority Data

(31) 4420764.6 (32) 15.06.1994 (33) DE

(71) Applicant(s)

Sandoz Ltd

(Incorporated in Switzerland)

35 Lichtstrasse, CH-4002 Basle, Switzerland

(72) Inventor(s)

Roland Wald

Markus Gisler

(74) Agent and/or Address for Service

B A Yorke & Co

Coomb House, 7 St John's Road, Isleworth,

Middlesex, TW7 6NH, United Kingdom

(51) INT CL<sup>6</sup>

C09B 47/08 47/04

(52) UK CL (Edition O )

C4P PCB PCB01P PC10 PC64 PC71 PC73 PC99 P116

(56) Documents Cited

US 4530924 A US 4368053 A US 4318883 A

(58) Field of Search

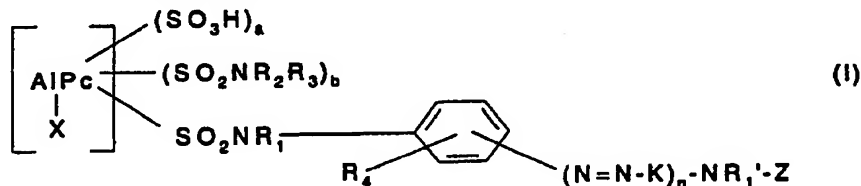
UK CL (Edition N ) C4P PCB

INT CL<sup>6</sup> C09B 47/04 47/08

ONLINE DATABASES: WPI, CLAIMS, EDOC, WPIL

(54) Aluminium-Phthalocyanine reactive dyes

(57) The aluminium-phthalocyanine reactive dyes of formula I

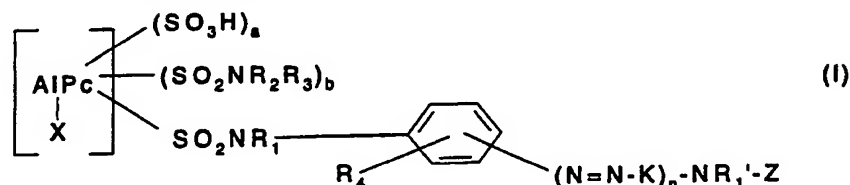


wherein the symbols Pc, X, R<sub>1</sub>, R<sub>1</sub>', R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, K, Z, a, B and n possess the significances given in claim 1 and claim 2, are eminently suitable for dyeing and printing hydroxyl-group-containing or nitrogen-containing organic substrates.

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Aluminium-phthalocyanine reactive dyes

The invention relates to the aluminium-phthalocyanine reactive dyes of formula I



and their salts

wherein

Pc signifies a phthalocyanine radical,

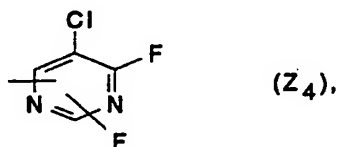
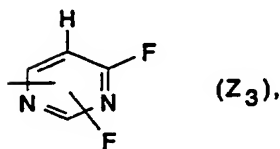
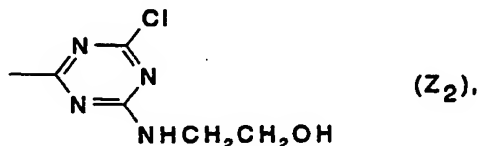
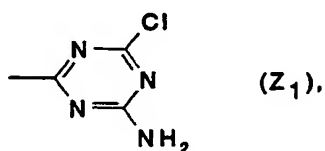
X signifies a chlorine atom or a hydroxyl group,

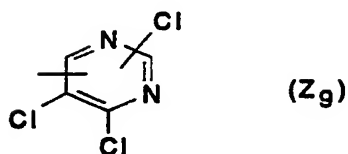
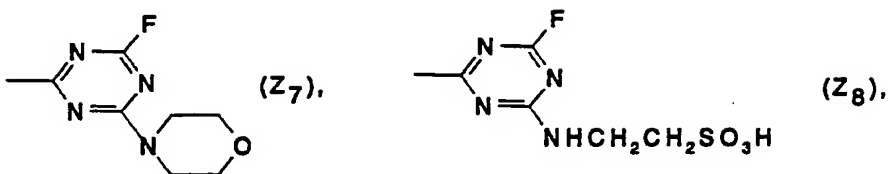
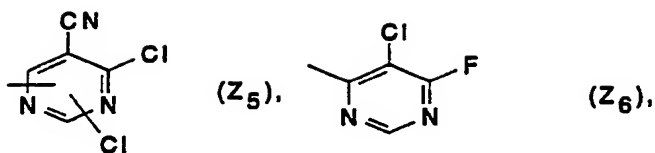
R<sub>1</sub> and R<sub>1</sub>' , independently of one another, signify hydrogen, or alkyl which may be substituted by a hydroxyl, halogen, -SO<sub>3</sub>H, -OSO<sub>3</sub>H or -COOH,

R<sub>2</sub> and R<sub>3</sub> , independently of one another, signify hydrogen, or alkyl with 1, 2, 3, 4, 5 or 6 carbon atoms, or together signify a C<sub>4-5</sub>-alkylene chain which may therein contain -O- or -NH-,

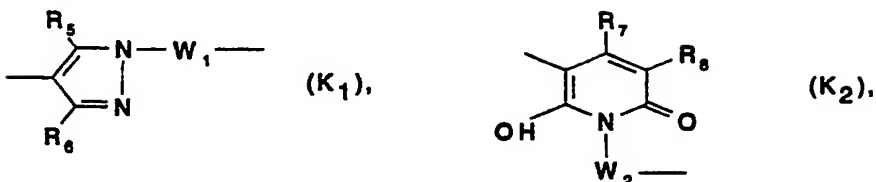
R<sub>4</sub> signifies hydrogen, halogen, hydroxyl, -COOH, -SO<sub>3</sub>H, alkyl or alkoxy,

Z is a heterocyclic fibre-reactive radical having one or two labile halogens selected from fluorine or chlorine, more preferably Z signifies a radical of formula Z<sub>1</sub> to Z<sub>9</sub>,





K signifies a radical of formula K<sub>1</sub> or K<sub>2</sub>



R<sub>5</sub> signifies a hydroxyl or amino group,

R<sub>6</sub> signifies alkyl, e.g., methyl or COR<sub>9</sub>,

R<sub>7</sub> signifies hydrogen, alkyl, C<sub>6</sub>-cycloalkyl, phenyl or phenylalkyl, wherein the phenyl radical and the phenylalkyl radical may bear up to 3 substituents, including up to three from the group consisting of halogen or alkyl, up to two from the groups -COOH or -SO<sub>3</sub>H and/or one from the group alkoxy, COR<sub>9</sub>, -alkylene-SO<sub>3</sub>H, alkylene-O-SO<sub>3</sub>H or alkylene-COR<sub>9</sub>. R<sub>7</sub> is preferably C<sub>1-2</sub>-alkyl, more preferably methyl,

R<sub>8</sub> signifies hydrogen, -CN, -CONH<sub>2</sub> or -SO<sub>2</sub>NH<sub>2</sub>, preferably hydrogen, each R<sub>9</sub>, independently of one another, signifies a hydroxyl, amino or alkoxy group,

- $W_1$  signifies a divalent bridging member which may be an alkylene group having from 2 to 4 carbon atoms, e.g., propylene, or an arylene group, preferably phenylene or stilben-4,4'-yl, wherein each of the phenylene nuclei of the divalent bridging members may bear a substituent, preferably a  $-SO_3H$  group,
- $W_2$  signifies a divalent bridging member, preferably alkylene with 2, 3 or 4 carbon atoms, which may bear a hydroxyl group, or it signifies phenylene or  $C_{1-2}$ alkyl-phenylene, wherein the phenylene nuclei of these latter two divalent bridging members may bear a substituent which is preferably a  $-SO_3H$  group,
- a signifies 1, 2 or 3,
- b signifies 0, 1 or 2, and  $a + b$  is a maximum of 3, and
- n signifies 0 or 1,

wherein, if not otherwise indicated, all the said alkyl, alkoxy and alkylene radicals contain 1, 2, 3 or 4 carbon atoms. All these radicals, insofar as they contain more than 2 carbon atoms, may be straight-chain or branched. Here, it is preferable for neither two oxygen or nitrogen atoms, nor one oxygen atom and one nitrogen atom, to be bonded to a particular carbon atom.

Halogen is in general fluorine, chlorine, bromine or iodine, preferably chlorine or bromine, especially chlorine.

The compounds of formula I are usually mixtures of positional isomers, which are differentiated by the positions of the substituents on the phthalocyanine ring.

When  $R_1$  and  $R_1'$  independently of one another are alkyl it is preferable that they contain 1 or 2 C-atoms. When  $R_1$  and  $R_1'$  are substituted alkyl, it is preferable that they are  $C_{1-3}$ -alkyl and more preferably that they contain a substituent selected from the series hydroxy,  $-SO_3H$ ,  $-OSO_3H$  and  $-COOH$ , of which  $C_{2-3}$ hydroxyalkyl is particularly preferred.

Each  $R_1$  and  $R_1'$  independently of the other is preferably  $R_{1a}$ , wherein each  $R_{1a}$ ,

independently of one another, signifies hydrogen, methyl, ethyl,  $C_{2-3}$ hydroxyalkyl,  $-(CH_2)_pSO_3H$ ,  $-(CH_2)_pOSO_3H$  or  $-(CH_2)_qCOOH$ , wherein  $p$  is 1 or 2 and  $q$  is 1, 2 or 3.  $R_1$  is more preferably  $R_{1b}$ , wherein each  $R_{1b}$ , independently of one another, signifies hydrogen or methyl.

When  $R_2$  and  $R_3$  independently of one another represent an alkyl group they are preferably  $C_{1-4}$ -alkyl, more preferably methyl or ethyl. When  $R_2$  and  $R_3$  represent an alkylene chain which may therein contain  $-O-$  or  $-NH-$ , then together with the N-atom to which they are bonded, they preferably form a pyrrolidine, piperidine, morpholine or piperazine ring.

$R_4$  is preferably hydrogen, methyl, methoxy,  $-COOH$  or  $-SO_3H$ , more preferably hydrogen,  $-COOH$  or  $-SO_3H$ .

The phenylene nuclei in the bridging members  $W_1$  and  $W_2$  may bear, apart from the preferred  $-SO_3H$  group, e.g., a chlorine, methyl, methoxy, ethoxy or a carboxy group.

The group  $Z$  is preferably  $Z_1$ ,  $Z_3$  or  $Z_7$ , more preferably  $Z_1$ . In a dyeing process, the nature of the group  $Z$  employed depends upon the temperature at which dyeing is carried out. When the dyeing temperature is from 30 to 80 °C, preferably 50 to 80 °C, more preferably 50 to 60 °C, the group  $Z$  may be  $Z_3$ ,  $Z_4$ ,  $Z_5$ ,  $Z_7$  and  $Z_8$ , more preferably  $Z_3$  and  $Z_7$ . When the dyeing temperature is from 80 to 100 °C the group  $Z$  may be  $Z_1$ ,  $Z_2$ ,  $Z_6$  and  $Z_9$ , more preferably  $Z_1$ .

The compounds of formula I may be formed in their salt form.

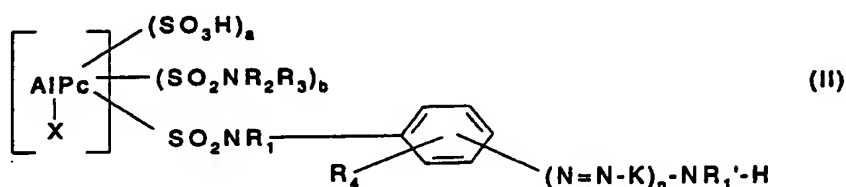
The constitution of the cation of the sulfo groups and optionally of carboxy groups that are additionally present in compounds of formula I, if they are in salt form, is not a vital factor, but may be any non-chromophoric cation which is conventional in the chemistry of reactive dyes, provided that, the corresponding salts fulfill the water solubility requirements.

Examples of suitable cations are alkali metal ions or unsubstituted or substituted ammonium ions, for example lithium, sodium, potassium, ammonium, mono-, di-, tri- and tetramethylammonium, triethylammonium and mono-, di- and tri-ethanolammonium.

Preferred cations are the alkali metal ions and the ammonium ion, of which sodium is particularly preferred.

In general, in a compound of formula I, the cations of the sulpho groups and optional carboxy groups may be the same or different and represent a mixture of the above-mentioned cations, i.e. the compound may also exist in mixed salt form.

The present invention further provides a process for the production of the compounds of formula I, their salts or mixtures thereof, wherein a compound of formula II



is condensed with a compound of formula III

Z-Hal

III,

wherein Hal is fluorine or chlorine, or with a mixture of such compounds of formula III.

The reaction of the compound of formula II with the compound Z-Hal is conveniently carried out at 0°-40°C, preferably 0°-20°C, and at pH 4-9, preferably

5-7. Water normally serves as the reaction medium.

Isolation of the compounds of formula I may be effected in a manner known in the art, e.g., the compounds may be separated from the reaction mixture by means of conventional salting out with alkali metal salts, filtered off and dried, optionally in a vacuum, at a slightly elevated temperature. Depending on the reaction and isolation conditions, a compound of formula I is obtained as a free acid or preferably in salt form or as a mixed salt, in which case it contains, for example, one or several of the above-mentioned cations. Salts or mixed salts may, however, also be converted from the free acid in a known manner, and vice versa, or a conventional exchange of salts may be undertaken.

The starting compounds of formula II or Z-Hal are either known or may be obtained from known starting materials using conventional syntheses.

The compounds of formula I their salts and mixtures thereof are reactive dyes; they are suitable for dyeing or printing hydroxy-group-containing or nitrogen-containing organic substrates.

Accordingly, in another aspect of the invention there is provided a process of dyeing or printing hydroxy-group-containing or nitrogen-containing organic substrates wherein the dyeing or printing is carried out with compounds as hereinabove described, their salts or mixtures thereof.

Preferred substrates which may be mentioned are leather and fibrous materials which consist of or contain natural or synthetic polyamides and in particular natural or regenerated cellulose, such as cotton, viscose or rayon staple fibre. The substrate which is usually preferred is textile material consisting of or containing cotton.

The compounds of formula I their salts or mixtures thereof may be employed in dye

baths or in printing pastes according to all the dyeing or printing processes which are customary for reactive dyes. Dyeing is preferably effected by the exhaust process from an aqueous medium and at a temperature range of 30-100°C, especially 50-60°C and 80-100°C. A goods-to-liquor ratio (substrate to liquor) of 1:6 to 1:30, preferably 1:10 to 1:20 is employed.

It is to be understood that any reference made above or hereinafter to compounds or salts in the plural is also to include reference to compound or salt in the singular.

In yet another aspect of the invention there is provided the use of compounds hereinabove defined, their salts or mixtures thereof in dyeing or printing substrates hereinabove described.

The compounds according to the invention may be used individually in a dyeing or printing process, or because of their good compatibility, also as a component in a combination dyeing or printing composition containing other reactive dyes of the same class, that is, reactive dyes which possess comparable dyeing properties, e.g., regarding all-round fastness, and exhaust value. The combination dyeings obtained have fastness which is comparable to that of dyeings made with individual dyes.

Accordingly in another aspect of the invention there is provided a combination dyeing or printing composition comprising a compound hereinabove described, its salt or mixtures thereof and dyestuffs of the same class.

In a further aspect of the invention there is provided a hydroxy-group-containing or nitrogen-containing organic substrate dyed or printed with compounds of the formula I, their salts or mixtures thereof.

Good exhaust and fixation values are obtained with the compounds of formula I. Any unfixed dye remaining after dyeing or printing is carried may be readily washed



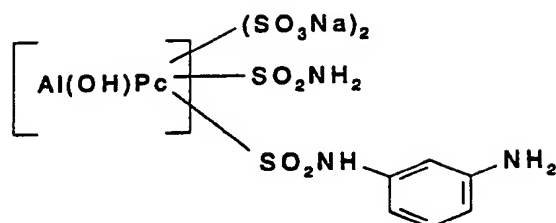
out. The dyeings and prints obtained have good light fastness. In addition, they have good wet fastness properties, e.g. to washing, water, sea water and perspiration, and have good resistance towards oxidative influences such as to chlorine-containing water, hypochlorite bleaches, peroxide bleaches and perborate-containing detergents.

The following examples serve to illustrate the invention. In the examples, the parts and percentages are by weight and the temperatures are given in degrees celsius.

#### **Example 1**

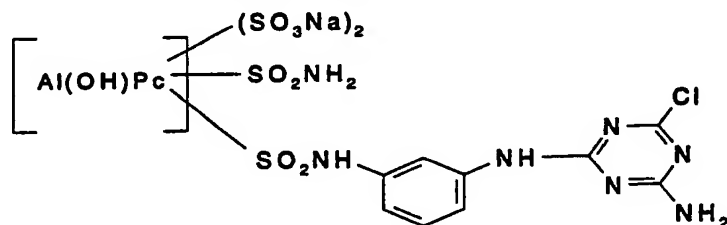
- a) 20 parts of  $\text{PcAlCl}_2\cdot 2\text{H}_2\text{O}$  were stirred in chlorosulphonic acid (140 parts) for 30 minutes at 20 to 25°C. The reaction mixture was then reacted to 135 to 140°C over 2 hours. After 4 hours the reaction mixture was cooled using an ice bath. The suspension thus formed was filtered and washed in ice water to remove excess acid.

97 g of the aluminium phthalocyanine sulphochloride produced according to the method described above were stirred into 300 ml of water and 100 g of ice, and then a solution consisting of 100 ml of ice-water and 14.5 g of 1,3-diaminobenzene monohydrochloride were added. The pH value was ca. 1-2. The pH was adjusted to 4 with 20% caustic soda solution, and a temperature of around 0-5°C was maintained for 4 hours. Prior to adding 7 ml of a 25% ammonia solution, the pH value was adjusted to 7.0 with 20% caustic soda solution. The mixture was stirred for 10 hours without cooling at pH 7 to 8, which was maintained by adding 20% caustic soda solution. The pH value was then adjusted to 10-11 and stirring was effected for 2 hours at 60°, before precipitating the intermediate product with sodium chloride and thereafter filtering off the precipitate. The compound thus obtained corresponds to formula



- b) The intermediate product obtained according to a) was dissolved in 600 ml of ice-water and mixed with 18.4 g of cyanuric chloride with stirring. The pH value was maintained for 3 hours at 6-6.5 using 20% caustic soda solution, thereafter 7 ml of a 25% ammonia solution was added dropwise. After 4 hours, the resultant dyestuff was precipitated by adding sodium chloride, filtered off and dried in a vacuum at 40-50°.

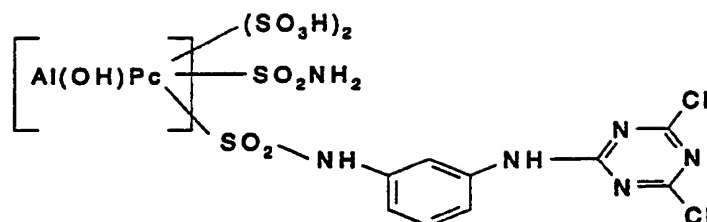
The dyestuff thus obtained corresponds to formula



The compound thus produced dyed cellulosic material, and in particular cotton, in brilliant green shades. The dyeings thus obtained have excellent wet fastness.

### Example 2

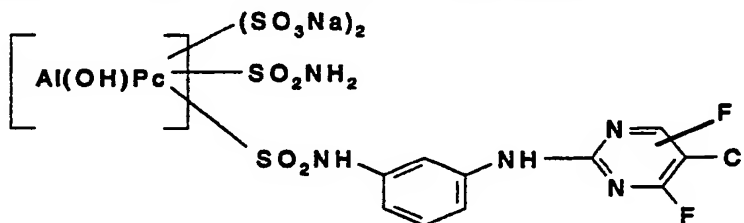
The process was effected according to the method of Example 1b with a modification such that the ammonia solution was not added. Work-up of the dyestuff was effected by precipitation with sodium chloride and subsequent filtration.



The compound of the above formula was thus obtained.

### Example 3

The process was effected according to the method of Example 1b with a modification such that the ammonia solution was not added, and instead of the cyanuric chloride mentioned in Example 1b), 17 g of 5-chloro-2,4,6-trifluoropyrimidine were used. The dyestuff of the formula

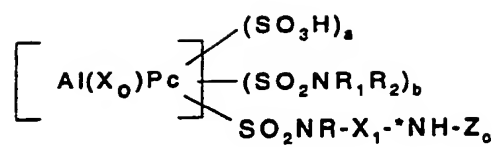


was thus obtained.

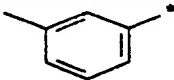
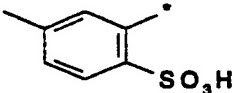
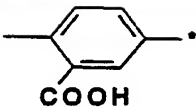
It dyes cotton in brilliant green shades with a high level of fastness.

### Examples 4-15

Further aluminium phthalocyanine compounds may be produced according to processes analogous to the methods described in Examples 1 to 3:



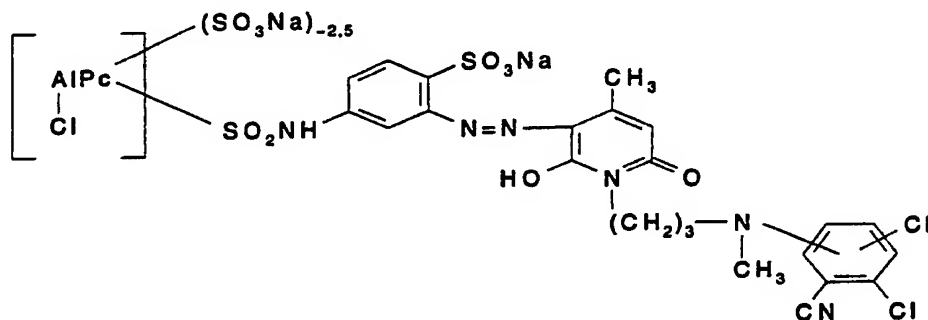
$\text{X}_0 = \text{Cl}$  or  $\text{OH}$ ;  $\text{Z}_0$  corresponds to formulae  $\text{Z}_1\text{-Z}_8$  (above).

Ex. No.	a	b	R <sub>1</sub>	R <sub>2</sub>	X <sub>1</sub>	Z <sub>0</sub>
4	1.5	1	H	H		Z <sub>1</sub>
5	1.7	1	H	CH <sub>2</sub> CH <sub>2</sub> OH	-do-	Z <sub>2</sub>
6	1.7	1	H	H	-do-	Z <sub>3</sub>
7	1.5	1	H	H	-do-	Z <sub>4</sub>
8	1.5	1	H	H	-do-	Z <sub>5</sub>
9	2	1	CH <sub>2</sub> CH <sub>2</sub> OH	CH <sub>2</sub> CH <sub>2</sub> OH	-do-	Z <sub>6</sub>
10	2.5	0	-	-	-do-	Z <sub>7</sub>
11	1.5	1	H	H	-do-	Z <sub>2</sub>
12	1.7	1	H	H		Z <sub>1</sub>
13	2.5	0	-	-	-do-	Z <sub>2</sub>
14	1.7	1	H	H		Z <sub>4</sub>
15	1.5	1	H	H	-do-	Z <sub>3</sub>

### Example 16

92 parts of the dyestuff base according to Example 13 (produced by sulphochlorinating aluminium phthalocyanine, and subsequently reacting it with 1,3-diaminobenzene-4-sulphonic acid, wherein the dyestuff base contains per molecule ca. 2.5 sulphonic acid groups and 1 sulphamide group) were stirred into 550 parts of water together with 7 parts of sodium nitrite. The solution which was cooled to 0-2°C was added in dropwise to 100 parts of ice/water and 60 parts of 30% hydrochloric acid. Whilst maintaining a temperature of 0-5°C, the diazonium salt suspension obtained was passed into a solution consisting of 300 parts of ice/water

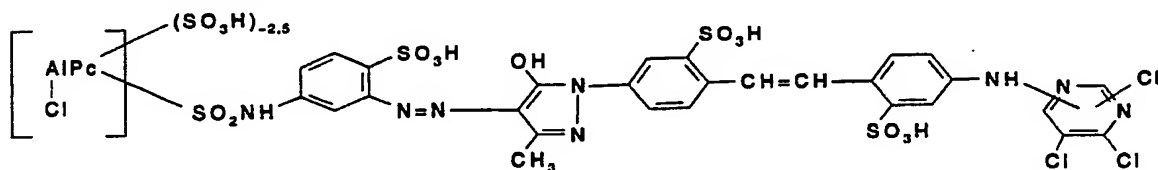
and 20 parts of 1-(3'-methylaminopropyl)-6-hydroxy-4-methylpyridone-(2). During the coupling reaction, the pH was held at 6.5-7.5 by adding 20% caustic soda solution. The resultant green solution was mixed at 20-35°C with 24 parts of 5-cyano-2,4,6-trichloropyrimidine. The pH was held at 7.5-8.0 by continuously adding 20% soda solution. After 3-4 hours, the reaction was complete. The solution was salted out with sodium chloride, the dyestuff precipitate filtered off by suction and dried at 40°C. The dyestuff obtained has the formula



and dyes cellulosic material, and in particular cotton, in brilliant green shades. Dyeings obtained from this dyestuff display excellent wet fastness.

### Example 17

The dyestuff, which in the form of the free acid corresponds to formula



may be produced and isolated according to a method analogous to that described in Example 16, using corresponding starting compounds. With this dyestuff, brilliant green cotton dyeings, which have good wet fastness, are obtained.

In the following table are listed the absorption maxima ( $\lambda_{\max}$  in nm) for the dyestuffs of the Examples. The measurements were made in water.

Ex. No.	$\lambda_{\max}$ (PC)
1b	670
2	670
3	670
4	668
5	670
6	670
7	668
8	668
9	672
10	674
11	668
12	672
13	674
14	669
15	667
16	672
17	672

The following examples are illustrative of the application of the above-mentioned dyestuff.

#### **Application Example A**

A dye bath consisting of 1000 parts of demineralised water, 80 parts of Glauber's salt (calcined), 1 part of sodium salt of 1-nitrobenzene-3-sulphonic acid and 2 parts of the dyestuff from Example 1b was heated over the course of 10 minutes to

80°C. Thereafter, 100 parts of mercerized cotton were added. Dyeing was effected for 5 minutes at 80°C, and heating was effected to 95°C over 15 minutes. After 10 minutes at 95°C, 3 parts of soda were added, after 20 minutes a further 7 parts of soda, and after 30 minutes at 95°C another 10 parts of soda were added. Dyeing subsequently continued for 60 minutes at 95°C. The dyed material was then removed from the dye bath, rinsed for 2 minutes in running, demineralised water of 60° ± 10°. It was then washed twice for 10 minutes, each time in 5000 parts of boiling, demineralised water, subsequently rinsed for 2 minutes in running, demineralised water of 60°C ± 10°C, 1 minute in running tap water of 60°C ± 10°C and for 1 minute in cold tap water. After drying, a brilliant green cotton dyeing with good fastness was obtained.

#### **Application Example B**

A dye bath consisting of 1000 parts of demineralised water, 80 parts of Glauber's salt (calcined) and 2 parts of the dyestuff from Example 3 was heated to 60°C over the course of 10 minutes. Then, 100 parts of mercerized cotton were added. After 25 minutes at 60°C, 0.7 parts of soda were added, after 20 minutes a further 1.3 parts of soda, and after 30 minutes at 60°C another 2 parts of soda were added. The bath was subsequently heated to 80°C over the course of 15 minutes, and dyeing continued for 60 minutes at 80°C. The dyed material was then removed from the dye bath, rinsed for 2 minutes in running, demineralised water of 60°C ± 10°C and for 1 minute in running tap water of 60°C ± 10°C. It was then washed twice for 10 minutes, each time in 5000 parts of boiling, demineralised water, subsequently rinsed for 2 minutes in running, demineralised water of 60°C ± 10°C, 1 minute in running tap water of 60°C ± 10°C and for 1 minute in cold tap water. After drying, a brilliant green cotton dyeing with good fastness was obtained.

The dyestuffs of Examples 4 to 17 or dyestuff mixtures of Examples 1b to 17 may also be used for dyeing cotton according to the method described in Examples A and B. Brilliant green dyeings were obtained, which have good fastness properties.



### **Application Example C**

A printing paste having the components

40 parts of the dyestuff of Example 1b

100 parts of urea

330 parts of water

500 parts of a 4% sodium alginate thickener

10 parts of sodium salt of 1-nitrobenzene-3-sulphonic acid and

20 parts of soda

1000 parts in all

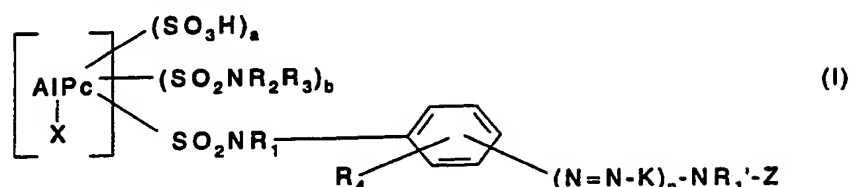
was applied to cotton material by a conventional printing process.

The printed and dried material was steamed for 4-8 minutes at 102-105°C and then given a cold and a hot rinse. The fixed cotton material was subsequently washed at the boil (analogously to Example A) and dried. The green print obtained had good all-round fastness.

The dyestuffs of Examples 2 to 17 were also used for printing cotton according to a method of Example C. In all cases, brilliant green prints with good fastness properties were obtained.

# CLAIMS

## 1. Aluminium-phthalocyanine reactive dyes of formula I



and their salts

wherein

Pc signifies a phthalocyanine radical,

X signifies a chlorine atom or a hydroxyl group,

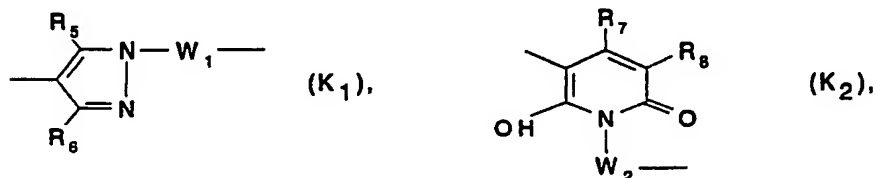
R<sub>1</sub> and R<sub>1</sub>' , independently of one another, signify hydrogen, or alkyl which may be substituted by an hydroxyl, halogen, -SO<sub>3</sub>H, -OSO<sub>3</sub>H or -COOH,

R<sub>2</sub> and R<sub>3</sub> , independently of one another, signify hydrogen, or alkyl with 1, 2, 3, 4, 5 or 6 carbon atoms, or together signify a C<sub>4-5</sub>-alkylene chain which may therein contain -O- or -NH-,

R<sub>4</sub> signifies hydrogen, halogen, hydroxyl, -COOH, -SO<sub>3</sub>H, alkyl or alkoxy,

Z is a heterocyclic fibre-reactive radical having one or two labile halogens selected from fluorine or chlorine,

K signifies a radical of formula K<sub>1</sub> or K<sub>2</sub>



R<sub>5</sub> signifies a hydroxyl or amino group,

R<sub>6</sub> signifies alkyl or COR<sub>9</sub>,

R<sub>7</sub> signifies hydrogen, alkyl, C<sub>6-6</sub>-cycloalkyl, phenyl or phenylalkyl, wherein the

phenyl radical and the phenylalkyl radical may bear up to 3 substituents, including up to three from the group consisting of halogen or alkyl, up to two from the groups -COOH or -SO<sub>3</sub>H and/or one from the group alkoxy, COR<sub>9</sub>, -alkylene-SO<sub>3</sub>H, alkylene-O-SO<sub>3</sub>H or alkylene-COR<sub>9</sub>,

R<sub>8</sub> signifies hydrogen, -CN, -CONH<sub>2</sub> or -SO<sub>2</sub>NH<sub>2</sub>,

each R<sub>9</sub>, independently of one another, signifies an hydroxyl, amino or alkoxy group,

W<sub>1</sub> signifies a divalent bridging member, selected from an alkylene or arylene group

W<sub>2</sub> signifies a divalent bridging member selected from an alkylene group with 2, 3 or 4 carbon atoms, which may bear a hydroxyl group, or it signifies phenylene or C<sub>1-2</sub>alkyl-phenylene,

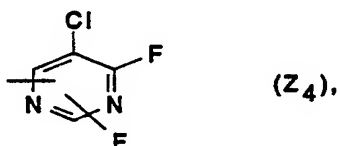
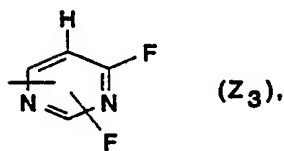
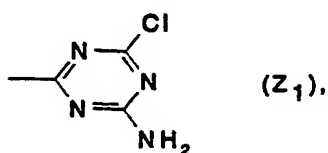
a signifies 1, 2 or 3,

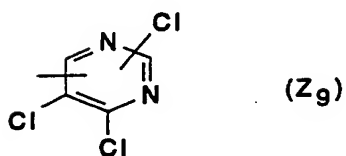
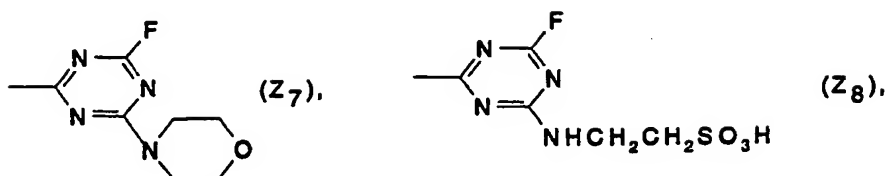
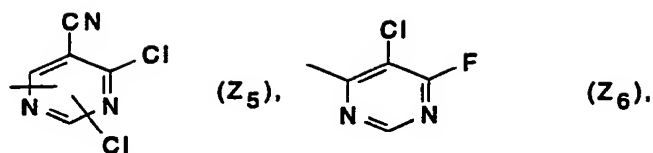
b signifies 0, 1 or 2 and a + b is a maximum of 3, and

n signifies 0 or 1,

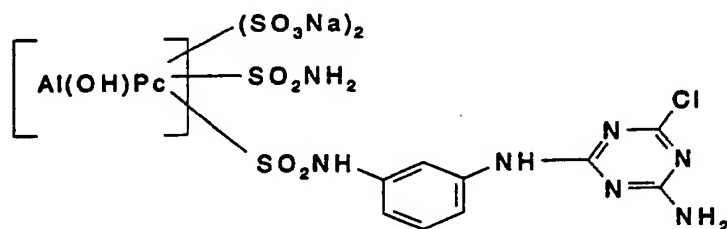
wherein, if not otherwise indicated, all the said alkyl, alkoxy and alkylene radicals contain 1, 2, 3 or 4 carbon atoms.

2. Aluminium-phthalocyanine reactive dyes according to claim 1 and their salts wherein Z signifies a radical of formula Z<sub>1</sub> to Z<sub>9</sub>,

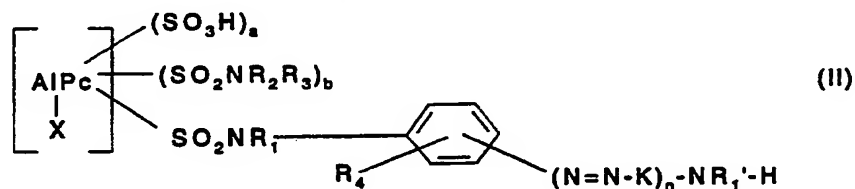




3. Aluminium-phthalocyanine reactive dyes according to claim 1 or claim 2 wherein R<sub>7</sub> is methyl or ethyl and R<sub>8</sub> is hydrogen.
4. Aluminium-phthalocyanine reactive dyes according to any of the claims 1 to 3 wherein W<sub>1</sub> represent a divalent bridging member which is phenylene or stilben-4,4'-yl and W<sub>2</sub> represents a divalent bridging member which is phenylene or C<sub>1-2</sub>-alkyl-phenylene wherein each of the phenylene nuclei of the divalent bridging members bears a -SO<sub>3</sub>H group.
5. Aluminium-phthalocyanine reactive dye according to claim 1 or claim 2 having the formula



6. Aluminium-phthalocyanine reactive dyes as defined in any of the claims 1 to 4 with reference to any of the Examples 1 to 17.
7. A combination dyeing or printing composition comprising a compound according to claim 1 to claim 6, their salts or mixtures thereof and other reactive dyes of the same class.
8. Process for the production of the aluminium-phthalocyanine reactive dyes of formula I, wherein a compound of formula II



is condensed with a compound of formula III

Z-Hal

III,

wherein Hal is fluorine or chlorine, or with a mixture of such compounds of formula III.

9. A process of dyeing or printing hydroxy-group-containing or nitrogen-containing organic substrates wherein the dyeing or printing is carried out with compounds as hereinabove described, their salts or mixtures thereof.
10. A process according to claim 9 wherein the hydroxy-group containing a nitrogen-containing organic substrate is a textile material consisting of or containing cotton.
11. A hydroxy-group-containing or nitrogen-containing organic substrate dyed or

printed with a compound according to any of the claims 1 to 6, their salts or mixtures thereof.

12. The use of compounds according to claim 1 to 6, their salts or mixtures thereof in dyeing or printing of hydroxy-group-containing or nitrogen-containing organic substrates.

Application No: GB 9511863.4  
Claims searched: 1-12

Examiner: Dr. A.J.Rudge  
Date of search: 7 September 1995

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.N): C4P(PCB)

Int Cl (Ed.6): C09B-047/08;-047/04

Other: ONLINE DATABASES: WPI, CLAIMS, EDOC, WPIL

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
A	US4548610 (Ciba-Geigy) - see the claims	1-12
X	US4530924 (Ciba-Geigy) - see claim 1	1 at least
X	US4318883 (Ciba-Geigy) - see claim 5	"

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.